



Preparing two-dimensional nano-catalytic combustion patterns using direct inkjet printing



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HIGHLIGHTS

- We demonstrate direct fabricating of two-dimensional catalytic combustion patterns.
- IJP method realized ultra low loading and high utilizing of Pt catalysts.
- Spontaneous combustion is achieved at room temperature and small scale (~800 μm).
- Accurate temperature control makes the catalyst an adjustable power source.

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ABSTRACT

Two-dimensional catalytic combustion patterns, which can be used as heat source in micro-nano scale MEMS devices such as gas sensor and micro-generator, are fabricated by inkjet printing (IJP). The performances of the catalytic patterns are evaluated by both traditional catalytic activity measurement and infrared thermography (IR) camera. Results show that ultra-low (0.014 mg cm^{-2}) loading and high utilizing ($34,710 \text{ mW mg}^{-1}$) of Pt catalysts can be achieved by inkjet printing method. Spontaneous combustion is also observed for the printed Pt/ Al_2O_3 powder membrane at rather low initiation temperature and small scale. The IR camera analysis indicates the uniform temperature distribution and rapid temperature response of the micro-patterned catalyst surface. With the advantages of the inkjet printing, this new direct-write method would, in principle, open up possibilities of these special catalyst patterns serving as micro energy sources for MEMS applications.

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1. Introduction

Micro heater fabricated by MEMS technology, possessing advantages of small size, fast thermal response, high temperature at low power consumption, has gained specific attention as they are key constituent parts in micro-sensors such as wind sensors [1], humidity sensors [2] and gas sensor [3]. Another kind of heat source at small scale is catalytic combustor, normally used in micro-

machined thermoelectric hydrogen sensors (micro-THS) [4–6]. Unlike the MEMS-based micro heater converting electric energy into stable heat energy, the catalytic combustor turn chemical energy into heat at low combustion temperature with extraordinary high energy density [7]. Furthermore, lower combustion temperature of catalytic combustion makes thermal stresses and heat losses less problematic [8]. Still, catalytic combustion acting as power supply for MEMS devices remains difficult, owing to the obstacles of reducing catalyst size below 1 mm^2 , shape controlling, uniform temperature distribution on catalyst surface and self-ignition of catalyst at room temperature.

Traditional ways like screen printing have been investigated for catalyst deposition. Although screen printing is a simple, cost-

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effective coating technique, this method do have disadvantages like uniformity, direct-contact of printing surface which may bring damage to the fragile device structure when applying in MEMS. Furthermore, screen printing is not qualified for ultra low ($<0.5 \text{ mg cm}^{-2}$) condition. Inkjet printing (IJP) is a technology for micro scale patterning, jetting solutions or turbid liquid with small particle size onto addressable sites on a specific substrate, flexible or inelastic. It has been considered as an alternative of lift-off process, since inkjet printing can achieve direct patterning without any masks at small scale [9]. It also has promising prospects in fields such as organic field-effect transistors (OFETs) [10], conductive features [11,12], sensor [13], polymer light-emitting diode (PLED) [14,15], radio frequency identification (RFID) tags [16], and fuel cell [17,18], etc. In general, it's more controllable, material saving and compatible with MEMS devices.

In this paper, we develop a rapid prototyping technique to fabricate Pt nano-catalytic patterns for use as a micro heater in MEMS devices. Chloroplatinic acid solution was chosen as the catalyst precursor ink to produce catalyst patterns at pre-defined position with different shapes. Catalysts characteristics including catalytic activity, catalytic combustion performance, temperature distribution and temperature response rate were investigated.

2. Experimental

2.1. Catalyst preparation and patterning

Platinum catalysts for low temperature methanol catalytic combustion were synthesized in situ on substrates via inkjet printing. An inkjet printable solution containing platinum ions was prepared by dissolving the commercially available chloroplatinic acid powder in water. Concentration of the printing ink was 0.01 mol L^{-1} . The chloroplatinic solution was then filtered three times by filter (pore size $0.45 \mu\text{m}$) after stood for 48 h to prevent nozzle clogging. Catalyst precursor solution was then printed on the heated substrates with special shape and defined loading.

The inkjet printer used as micropatterning tool in this experiment was a commercial Autodrop micro dispensing system (Microdrop Technologies GmbH, Germany), which is for non-contact dispensing of liquids in single droplets of volume ranges from 20 pl to 380 pl. The picture of microdrop jetting system and schematic of ink jetting is shown in Fig. 1. The inner diameter of nozzles is $70 \mu\text{m}$. Applied voltage and pulse width are two key factors to determine the printability and dimensions

of the droplets [19]. Low voltage can't provide enough energy for droplets to be jetted. Conversely, higher applied voltage will results in the formation of satellite droplets, which are detrimental to the precisely control of catalyst amount and shape. A similar behavior can also be observed when changing the applied pulse width. Substrates are placed on the x - y - z table, which has a positioning accuracy of $5 \mu\text{m}$. A stroboscopic camera was used to study the behavior of droplets between the nozzle and substrate.

Different amount and shape of the catalyst can be obtained by controlling the ink jetting process and the movement of the x - y - z table, thus different patterns were fabricated (Fig. 2). Optimum conditions of the voltage and pulse width were adopted here, which were 50 V and $24 \mu\text{s}$ respectively. The droplets were jetted from nozzle without satellite droplets with a flight speed of 1 m s^{-1} and diameter of $70 \mu\text{m}$. Then printed arrays were reduced in methanol flow at 400°C for 1 h to obtain platinum catalyst patterns, after which the color of printed arrays changed from yellow to black (in web version), indicating the formation of Pt.

2.2. Measurements of methanol catalytic combustion

The morphology of printed catalytic was evaluated by 3D microscope (VHX-600E, Keyence) to determine the size and uniformity of platinum catalyst.

Catalytic activity measurements were carried out to determine catalytic performance of prepared platinum catalyst. Samples were placed in center of a reactor ($8 \times 3.5 \times 0.5 \text{ cm}^3$) under flowing 10 vol. % of methanol in air at different temperature to elucidated the conversion rate of methanol. The flow rate of air was 3 ml min^{-1} . The gas before and after reaction were analyzed on line by gas chromatograph (GC2060, Ramiin) with a flame ionization detection (FID) detector.

Methanol catalytic combustion performance of printed platinum catalysts was tested in a stainless reactor. Sealed chamber reactor with infrared transparent CaF_2 was designed to observe the oxidation reaction of methanol on catalytic surface, as shown in Fig. 3(a). The gas flow rates were regulated by a flow controller. An IRM-320 infrared thermographic camera (Shanghai Infrared Optoelectronics Technology, China) was used to observe the temperature profiles of inkjet printed catalyst patterns. This infrared thermographic camera has been demarcated by a certificated blackbody source (HFY-300A, Shanghai Institute of Technical Physics), and the temperature resolution is 2°C . Fig. 3(b) shows the 2-D and 3-D infrared pictures of printed catalyst.

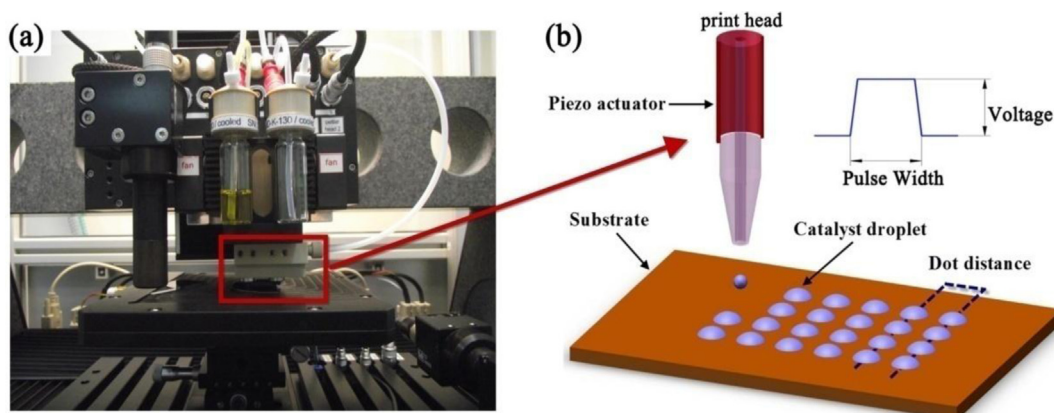


Fig. 1. Picture of microdrop jetting system (left) and schematic of ink jetting (right).

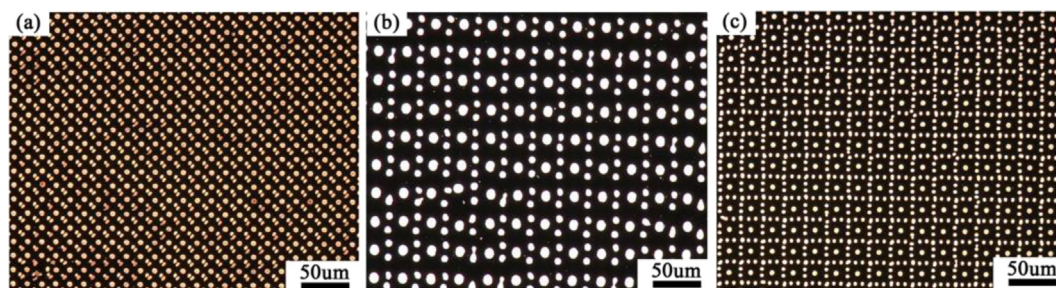


Fig. 2. Optical micrographs of different catalytic patterns.

3. Results and discussion

3.1. Measurement of micro-patterned methanol catalytic combustion

High methanol conversion and low energy dissipation are two key factors to acquire high temperature raise on catalyst surface at small scale, requiring excellent catalytic activity and low thermal conductivity substrate. Two samples with different substrates, Si wafer and Al_2O_3 powder on glass, were fabricated to accomplish the catalytic activity measurements and infrared thermography (IR) measurements. Inkjet platinum catalysts for both two samples were 10×10 dot matrix containing 200 droplets each dot. The radius of one dot was $400 \mu\text{m}$, and thickness of Al_2O_3 layer was about $20 \mu\text{m}$.

Catalytic activity measurements were carried out to investigate the catalytic performance of printed Pt catalyst under different temperature. For comparison, another catalyst sample was fabricated by hand painting (HP) method on a Si Substrate. Here, the total amounts of Pt in all samples were the same controlled by the

volume and concentration of the solution. Both IJP-Si and IJP- Al_2O_3 show relative good catalytic activity at low temperature, shown in Fig. 4. The conversion rate of methanol increases, along with the increasing temperature. The conversion is over 80% when the flow rate of methanol was 3 ml min^{-1} for all IJP samples at 100°C . Moreover, the methanol conversion rates of IJP samples are almost twice that of HP, indicating the apparent advantage of IJP.

Total amount of each Pt catalyst dot can be calculated based on the numbers, volume of jetted droplets and concentration of the ink, which were 200, 179 pl and 0.01 mol L^{-1} , respectively. Platinum utilizing (mW mg^{-1}) is related to Platinum mass and the energy released on Pt surface during the catalyst process. An ultra-low Pt loading of 0.014 mg cm^{-2} were achieved by IJP in this experiment, which can hardly be done using HP method. As reported by Taylor etc [18], this ultra-low Pt loading would dramatically improve the platinum utilizing by nearly five times. Similar conclusion can be drawn here. The Pt utilization of IJP- Al_2O_3 under 100°C at this 0.014 mg cm^{-2} loading reaches up to $34,710 \text{ mW mg}^{-1}$. This value could be even higher since the drop counts can be reduced without decrease of the dot radius.

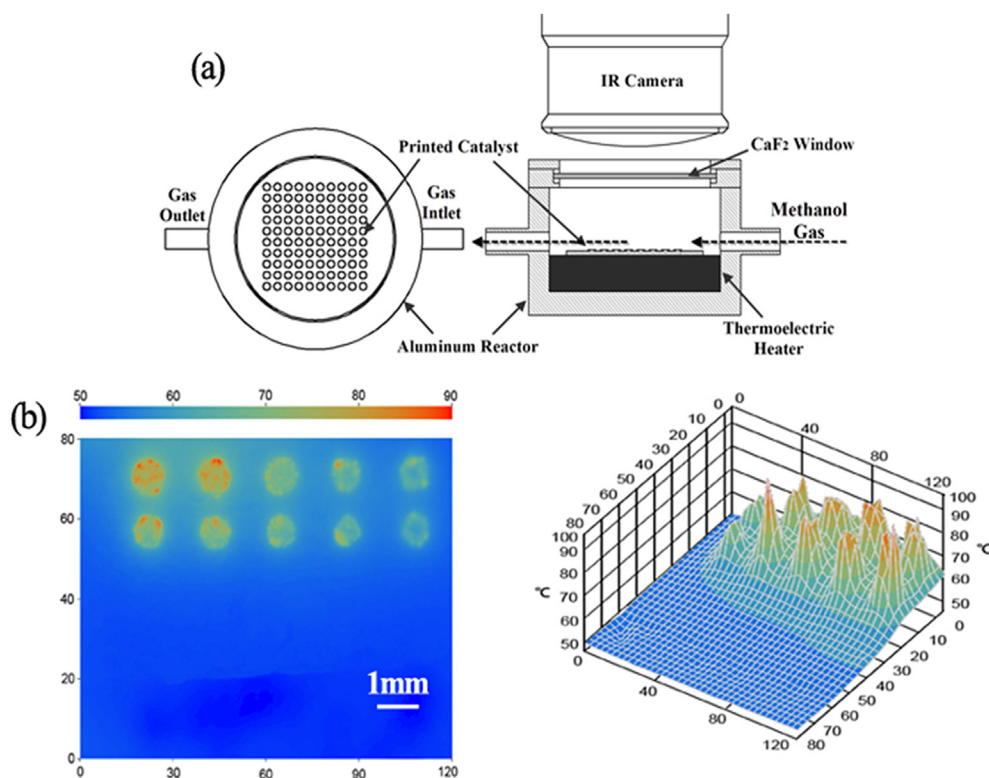


Fig. 3. (a) Schematic of reactor top (left) and side view (right); (b) the infrared thermographic image (left) and the three-dimensional temperature profile (right) of inkjet printed catalyst.

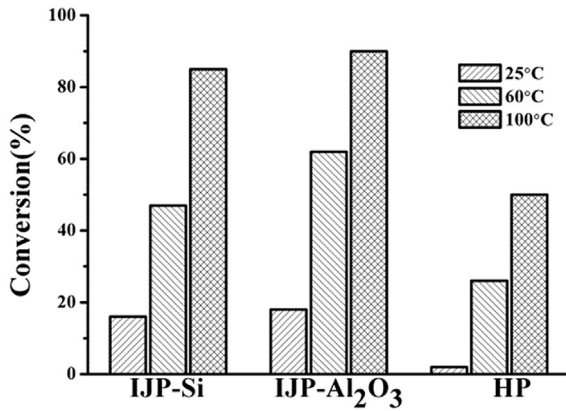


Fig. 4. The conversion of methanol over the platinum patterns printed on the Si substrate and Al_2O_3 powder at different reaction temperatures.

Temperature variations of the printed heat source were monitored by the infrared thermographic camera during the combustion process. For inkjet printed catalyst dots on the Si substrate, there is a descent of temperature on both substrate and the catalyst surface after methanol-air mixture reached the catalyst surface, as shown

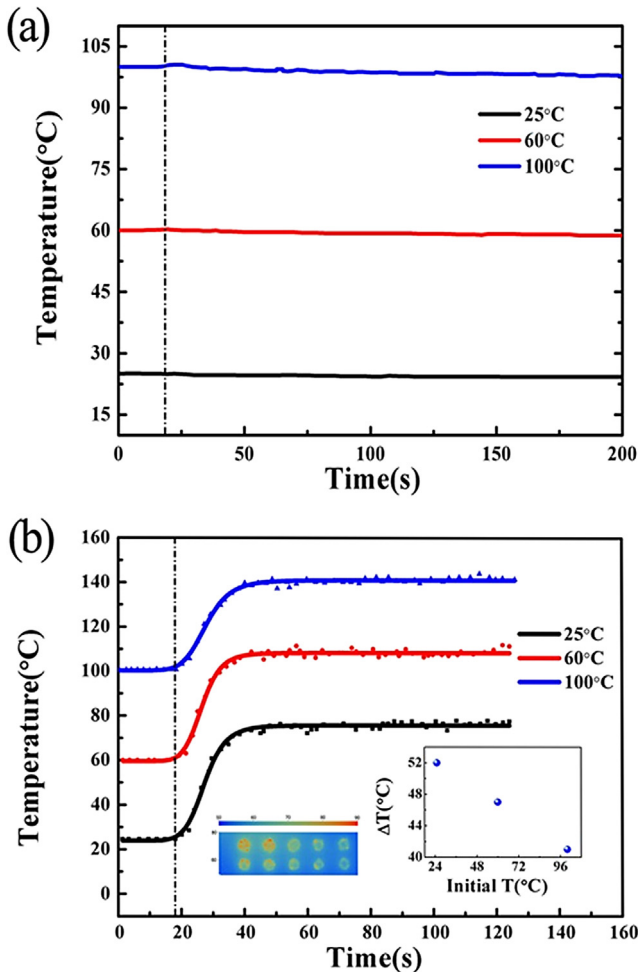


Fig. 5. The temperature variations of catalyst dots fabricated by overlap printing 200 droplets on Si substrate (a) and Al_2O_3 powder membrane (b) at different initial substrate temperatures. Zone I, without methanol gas; zone II, mixture of saturated methanol/air vapor at certain flow rate. The inset is the infrared thermographic image of catalyst dots fabricated by overlap printing 200 droplets during methanol catalytic combustion.

Table 1

Heat parameters during energy transfer processes on Si substrate.

| | 25 °C (mW) | 60 °C(mW) | 100 °C(mW) |
|-----------------|------------------------------------|------------------------------------|------------------------------------|
| Q | 25.9 | 76.2 | 137.8 |
| ΔQ_{cd} | $140 \times \Delta T$ | $121 \times \Delta T$ | $111 \times \Delta T$ |
| ΔQ_{cv} | $2 \times 10^{-5} \times \Delta T$ | $2 \times 10^{-5} \times \Delta T$ | $2 \times 10^{-5} \times \Delta T$ |
| ΔQ_{rd} | 0 | 12.8 | 33.3 |

in Fig. 5(a). The temperature of catalyst patterns drops slightly, i.e. about 1–2 °C. As for Al_2O_3 powder condition, the temperature raises prominently in a short time when the airflow passes through, shown in Fig. 5(b). The inset in Fig. 5(b) shows the infrared thermographic image of catalyst patterns, demonstrating the temperature of the catalyst region is much higher than that of the substrate. Furthermore, it can be seen in Fig. 5(b) that the highest temperature of catalyst surface increases with initial substrate temperature. A temperature rise of nearly 52 °C is obtained when initial substrate temperature is 25 °C, which means self-ignition is accomplished. This kind of self-ignited catalyst pattern can be used as heat source when applying to the cross-plane structure thermoelectric device [20]. Assuming the Seebeck efficiency is $100 \mu\text{V K}^{-1}$, the output of a single thermoelectric pillar, which has a diameter of 60 μm and height of 40 μm , is 100 μV with only 1 K temperature difference. That is 20 mV for a 200-series of thermoelectric pillars with an area no bigger than 1 cm^2 , manifesting great application prospect for thermoelectric generator (this part of work is already underway; preliminary positive results have shown the feasibility of power generator).

To understand the reason why these two samples have a totally different performance on the temperature distribution while the results of methanol conversion rate are nearly the same, we should analysis the energy transfer processes. In this work, the main energy transfer processes of the catalyst comprised four sections: exothermic reaction occurs on catalyst surface, heat conduction from catalyst to substrates, heat convection with methanol flow and the radiation. Energy produced by methanol exothermic reaction Q is the product of methanol combustion heat and the amount of methanol; Heat conduction is given by:

$$\Delta Q_{cd} = k A_{cd} \frac{(T_{\text{hot}} - T_{\text{cold}})}{\Delta x} \quad (1)$$

where k is thermal conductivity, A is conducting area and Δx is conducting length. Similarly, heat convection can be written as:

$$\Delta Q_{cv} = f A_{cv} v^{1/2} (T_{\text{hot}} - T_{\text{cold}}) \quad (2)$$

where A_{cv} is the heat transfer area, v is the matter flow velocity of methanol, and f is empirical coefficient ($\text{W m}^{-2}(\text{m s}^{-1})^{1/2} \text{K}$), which is $14.5 \text{ W m}^{-2}(\text{m s}^{-1})^{1/2} \text{K}^{-1}$ for gas flow.

Heat radiation can be written as:

$$\Delta Q_{rd} = \varepsilon \sigma A_{rd} (T_{\text{hot}}^4 - T_{\text{cold}}^4) \quad (3)$$

Table 2

Heat parameters during energy transfer processes on Al_2O_3 .

| | 25 °C (mW) | 60 °C (mW) | 100 °C (mW) |
|-----------------|------------------------------------|------------------------------------|------------------------------------|
| Q | 29.2 | 100.5 | 145.9 |
| ΔQ_{cd} | $12.5 \times \Delta T$ | $12.5 \times \Delta T$ | $12.5 \times \Delta T$ |
| ΔQ_{cv} | $2 \times 10^{-5} \times \Delta T$ | $2 \times 10^{-5} \times \Delta T$ | $2 \times 10^{-5} \times \Delta T$ |
| ΔQ_{rd} | 0 | 12.8 | 33.3 |

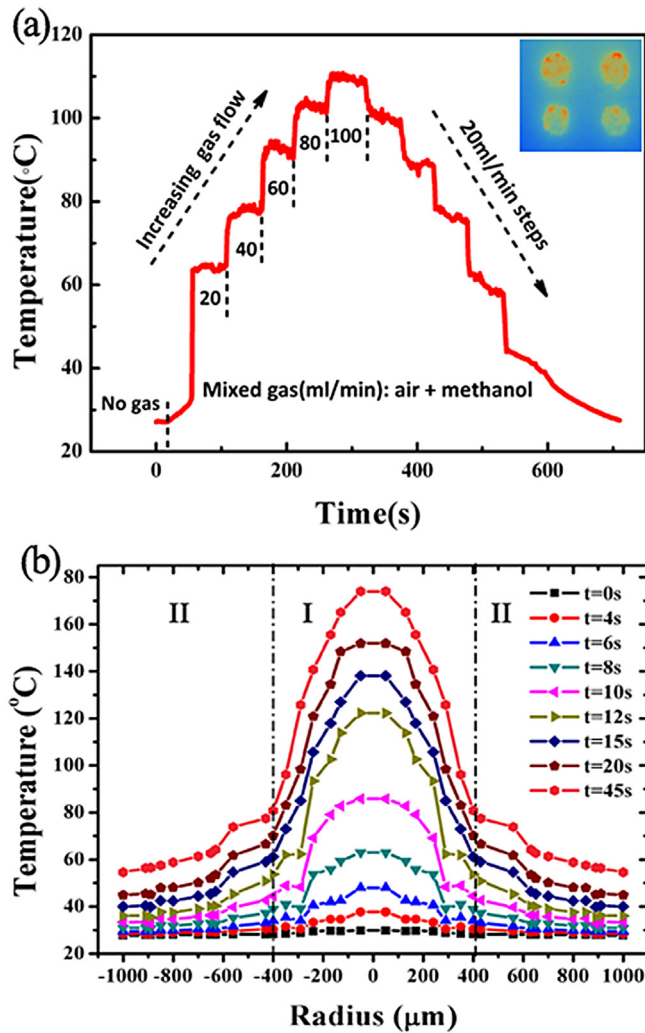


Fig. 6. (a) The temperature variations of catalyst dots under different gas flow rate. (b) Temperature distribution of an 800 μm -diameter catalyst dot at different time. I is the catalyst region; II is the substrate region near catalyst.

where A_{rd} is the heat radiation area, σ is the Stefan–Boltzmann constant equals $5.67 \times 10^{-8} \text{W m}^{-2} \text{K}^{-4}$, and ε is the emissivity, which should be less than 1 (emissivity of blackbody).

Temperature will rise when the velocity of energy accumulation Q is faster than dissipating, which means Q is greater than

$\Delta Q_{\text{cd}} + \Delta Q_{\text{cv}} + \Delta Q_{\text{rd}}$; conversely, temperature may stay the same or dropped down. For the case of 25 $^{\circ}\text{C}$, the value of Q is 25.9 mW (Table 1) on Si substrate and 29.2 mW (Table 2) on Al_2O_3 ; ΔQ_{cv} is several orders of magnitude smaller than ΔQ_{cd} , thus can be ignored; ΔQ_{rd} is proportional to $(T_{\text{hot}}^4 - T_{\text{cold}}^4)$, which can also be neglected at room temperature. As we can infer from tables above, no temperature raise would occur on Si substrate considering that the energy produced during the catalytic process is 25.9 mW while heat conduction is equal to $140 \times \Delta T \text{mW}$; for Al_2O_3 substrate, low energy dissipating indicates that temperature raise could be possible; this is also confirmed as shown in Fig. 5. The same conclusion can be drawn at 60 $^{\circ}\text{C}$ and 100 $^{\circ}\text{C}$.

The temperature variations of catalyst dots on the Al_2O_3 powder is related to gas flow rate at room temperature (Fig. 6(a)). When methanol piped in at the flow rate of 20 ml min^{-1} , the temperature rises tardily at first, indicating a process of heat accumulation; as temperature reaches to an appropriate value for catalytic reaction, heat accumulation intensifies dramatically, which lead to the quick temperature rise. This temperature soon reaches a limit when energy accumulation speed is rebalanced with the dissipating speed.

When the flow rate increases, the temperature of the catalyst surface enlarges correlatively, indicating the possibility of accurate temperature control. This means that the IJP catalyst patterns can be a power adjustable heat source. Temperature distribution of a catalyst dot with a diameter of 800 μm at different time is exhibited in Fig. 6(b), manifesting that catalyst combustion is observed at room temperature; temperature rises slowly at first 8 s, and after that rapid promotion of temperature takes place. Temperature of the substrate surface near catalyst hardly changes, indicating that this printed catalyst possesses low lateral energy loss thus high energy density.

Micro-scaled heat source pattern “SH” (SH stands for Shanghai) was fabricated by inkjet printing. Fig. 7(left) shows the IR image and microscopic image of the catalyst pattern. When the methanol gas reaches to the catalyst surface, spontaneous self-ignition combustion of methanol has been achieved. The uniformity of temperature distribution is relatively good as showed in Fig. 7(right), in spite of some localized temperature hot spots formed during unsteady inhomogeneous combustion. The heated zone is well focused on where catalyst is printed, which means such patterned catalyst can be used as a micro patterned heat source to heat specific zone of MEMS devices.

4. Conclusions

In this paper, micro catalyst patterns with controllable shape and loading were directly fabricated in situ using the platinum

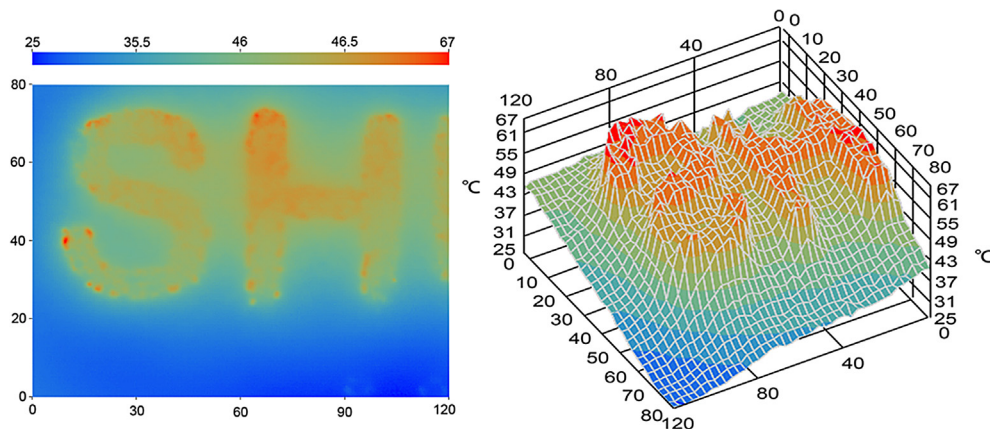


Fig. 7. The infrared thermographic image and of inkjet printed catalyst pattern (SH) during methanol catalytic combustion (left); The three-dimensional temperature profile of inkjet printed catalyst patterns “SH” (right).

precursor ink. To the best of our knowledge this is the first time a study such as this has been reported in the literature. Specially, ultra-low (0.014 mg cm^{-2}) loading and high utilizing ($34,710 \text{ mW mg}^{-1}$) of Pt catalysts is achieved by inkjet printing (IJP) method. On the basis of the results reported, by controlling the flow rate of mixed gas, the patterned catalyst becomes an adjustable power source, which could found use when localized heating at micro-scale is required.

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References

- [1] F. Mailly, A. Giani, R. Bonnot, P. Temple-Boyer, F. Pascal-Delannoy, A. Foucaran, A. Boyer, *Sens. Actuat. A* 94 (2001) 32–38.
- [2] C.-L. Dai, *Sens. Actuat. B* 122 (2007) 375–380.
- [3] Y.O. Yaowu Mo, Motoshi Tajima, Takehito Nakai, Nobuyuki Yoshiike, Kazuki Natukawa, *Sens. Actuat. B* 79 (2001) 175–181.
- [4] T. Okamasa, G.-G. Lee, Y. Suzuki, N. Kasagi, S. Matsuda, *J. Micromech. Microeng.* 16 (2006) S198–S205.
- [5] W. Shin, M. Nishibori, K. Tajima, L.F. Houlet, Y. Choi, N. Izu, N. Murayama, I. Matsubara, *Sens. Actuat. B* 118 (2006) 283–291.
- [6] W. Shin, K. Tajima, Y. Choi, N. Izu, I. Matsubara, N. Murayama, *Sens. Actuat. B* 108 (2005) 455–460.
- [7] S.T. Kazushi Yoshida, Shigeaki Tomonari, Daisuke Satoh, Masayoshi Esashi, *J. Microelectromech. Syst.* 15 (2006) 195–203.
- [8] Z. Hu, V. Boiadjev, T. Thundat, *Energy Fuels* 19 (2005) 855–858.
- [9] Y. Bai, S. Ho, N.A. Kotov, *Nanoscale* 4 (2012) 4393–4398.
- [10] H. Sirringhaus, *Science* 290 (2000) 2123–2126.
- [11] N. Komoda, M. Nogi, K. Suganuma, K. Kohno, Y. Akiyama, K. Otsuka, *Nanoscale* 4 (2012) 3148–3153.
- [12] J. Perelaer, C.E. Hendriks, A.W. de Laat, U.S. Schubert, *Nanotechnology* 20 (2009) 165303.
- [13] V. Penmatsa, T. Kim, M. Beidaghi, H. Kawarada, L. Gu, Z. Wang, C. Wang, *Nanoscale* 4 (2012) 3673–3678.
- [14] K.M. Tatsuya Shimoda, Shunichi Seki, Hiroshi Kiguchi, *MRS Bull.* 28 (2003) 821–827.
- [15] J.L. Shun-Chi Chang, Jayesh Bharathan, Yang Yang, Jun Onohara, Junji Kido, *Adv. Mater.* 11 (1999) 734–737.
- [16] D. Huang, F. Liao, S. Moles, D. Redinger, V. Subramanian, *J. Electrochem. Soc.* 150 (2003) G412.
- [17] S. Busato, A. Belloli, P. Ermanni, *Sens. Actuat. B* 123 (2007) 840–846.
- [18] A.D. Taylor, E.Y. Kim, V.P. Humes, J. Kizuka, L.T. Thompson, *J. Power Sources* 171 (2007) 101–106.
- [19] E. Tekin, P.J. Smith, S. Hoeppener, A.M.J. van den Berg, A.S. Sussha, A.L. Rogach, J. Feldmann, U.S. Schubert, *Adv. Funct. Mater.* 17 (2007) 23–28.
- [20] G.J. Snyder, J.R. Lim, C.K. Huang, J.P. Fleurial, *Nat. Mater.* 2 (2003) 528–531.